



January 24, 2000

Hon. Commissioner of Patents and Trademarks
Washington, DC 20231

Attention: Box PCT-DO/US

Sir: Re: International Application PCT/CH97/00475 filed December 19, 1997
Priority claimed: Swiss Application No. 3141/96 filed December 20, 1996
Inventors: Prof. René L.J. FLÜKIGER, et al.
Title: PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR
WITH SUPERCONDUCTING CORES, AND THUS MANUFACTURED
CONDUCTOR
Attorney Docket: 31506-149973

Submitted herewith under 35 USC 371(c) are the following documents for the purpose of entering the national stage for the United States:

- International Application PCT/CH97/00475 published as WO 98/28802, with international search report issued by the European Patent Office.

- Petition to Revive
- International application
- Translation of international application
- 3 sheets formal drawings
- Preliminary amendment to eliminate multiple claim dependency
- Inventor Declaration
- Assignment document with cover sheet
- Small-Entity Declarations (2)
- International Preliminary Examination Report



PCT/CH97/00475
January 24, 2000
Page 2

- Official fees:

Revival fee	\$605.00
Filing Fee	420.00
Assignment recordation fee	40.00

Total fees enclosed: \$ 1,065.00

Should no remittance be attached, or should a greater or lesser fee be required, please charge or credit Account No. 22-0261.

DESIGNATION OF CORRESPONDENCE ADDRESS

Please address all mailed communications to VENABLE, Post Office Box 34385, Washington DC 20043-9998.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Gabor J. Kelemen", written over a horizontal line.

Gabor J. Kelemen
Registration No. 21,016
VENABLE
Suite 1000
1201 New York Avenue NW
Washington, DC 20005-3917
Telephone: 202-962-4800
Telefax: 202-962-8300

Applicant or Patentee: René L.J. Flükiger et al.

Attorney Docket: 31506-149973

Application or Patent No.: PCT/CH97/00475

Filed or Issued: December 19, 1997

For: PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR WITH SUPERCONDUCTING CORES, AND THUS MANUFACTURED CONDUCTOR

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(b)) - INDEPENDENT INVENTOR

As the below named inventor, I hereby declare that I qualify as an independent inventor as defined in 37 C.F.R. § 1.9(c) for purposes of paying reduced fees under sections 41(a) and (b) of Title 35, United States Code, to the U.S. Patent and Trademark Office with regard to the invention entitled PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR WITH SUPERCONDUCTING CORES, AND THUS MANUFACTURED CONDUCTOR described in

☐ the specification filed herewith

☒ Application No. PCT/CH97/00475, filed December 19, 1997

☐ Patent No. _____, issued _____

I have not assigned, granted, conveyed, or licensed and am under no obligation under contract or law to assign, grant, convey, or license, any rights in the invention to any person who could not be classified as an independent inventor under 37 C.F.R. § 1.9(c) if that person had made the invention, or to any concern which would not qualify as a small business concern under 37 C.F.R. § 1.9(d) or a nonprofit organization under 37 C.F.R. § 1.9(e).

Each person, concern, or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

☐ no such person, concern or organization

☒ persons, concerns or organizations listed below*

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. 37 C.F.R. § 1.27.

NAME UNIVERSITÉ DE GENÈVE

ADDRESS: représentée par son DÉPARTEMENT DE PHYSIQUE DE LA MATIÈRE CONDENSÉE

24, quai Ernest-Ansermet, 1211 Genève 4, Switzerland

☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☒ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any changes in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. 37 C.F.R. § 1.28(b).

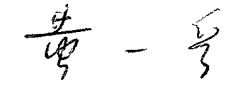
I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

Prof. René L.J. Flükiger
NAME OF INVENTOR


SIGNATURE OF INVENTOR

Geneva 24.11.99
DATE

Dr. Ybing (also known as Yibing) Huang
NAME OF INVENTOR


SIGNATURE OF INVENTOR

Wroclaw, 06/12/99
DATE

Dr. Giovanni Grasso
NAME OF INVENTOR


SIGNATURE OF INVENTOR

Geneva, 1.12.1999
DATE

Applicant or Patentee: René L.J. Flükiger et al. Attorney Docket: 31506-149973
Application or Patent No.: PCT/CH97/00475
Filed or Issued: December 19, 1997
For: PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR WITH SUPERCONDUCTING CORES, AND THUS
MANUFACTURED CONDUCTOR

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(d)) - NONPROFIT ORGANIZATION

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION UNIVERSITÉ DE GENÈVE
ADDRESS OF ORGANIZATION représentée par son DÉPARTEMENT DE PHYSIQUE DE LA MATIÈRE CONDENSÉE
24, quai Ernest-Ansermet, 1211 Genève 4, Switzerland

TYPE OF ORGANIZATION

☒ UNIVERSITY OR OTHER INSTITUTION OF HIGHER EDUCATION
☐ TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) AND 501(c)(3))
☐ NONPROFIT SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED STATES OF AMERICA
(NAME OF STATE _____)
(CITATION OF STATUTE _____)
☐ WOULD QUALIFY AS TAX EXEMPT UNDER INTERNAL REVENUE SERVICE CODE (26 USC 501(a) AND 501(c)(3)) IF
LOCATED IN THE UNITED STATES OF AMERICA
☐ WOULD QUALIFY AS NONPROFIT, SCIENTIFIC OR EDUCATIONAL UNDER STATUTE OF STATE OF THE UNITED
STATES OF AMERICA IF LOCATED IN THE UNITED STATES OF AMERICA
(NAME OF STATE _____)
(CITATION OF STATUTE _____)

I hereby declare that the nonprofit organization identified above qualifies as a nonprofit organization as defined in 37 CFR 1.9(e) for
purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code with regard to the invention entitled
PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR WITH SUPERCONDUCTING CORES, AND THUS
MANUFACTURED CONDUCTOR

by inventor(s) René L.J. Flükiger, Ybing (also known as Yibing) Huang, and Giovanni Grasso

described in

☐ the specification filed herewith
☒ application serial no. PCT/CH97/00475, filed December 19, 1997
☐ patent no. _____, issued _____

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the
above-identified invention.

If the rights held by the nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is
listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business
concern under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit
organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each named person, concern or organization
having rights to the invention averring to the status as small entities. (37 CFR 1.27)

None

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small
entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status
as a small entity is no longer appropriate. (37 CFR 1.28(b))

Applicant or Patentee: René L.J. Flükiger et al.
Application or Patent No.: PCT/CH97/00475

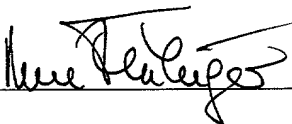
Attorney Docket: 31506-149973

- 2 -

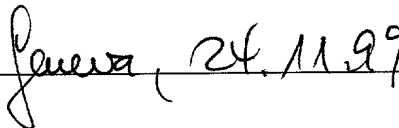
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING	<u>Prof. René L.J. Flükiger</u>
TITLE IN ORGANIZATION	<u>Executive Director</u>
ADDRESS OF PERSON SIGNING	<u>Département de Physique de la Matière Condensée</u>
	<u>24, quai Ernest-Ansermet</u>
	<u>1211 Genève 4, Switzerland</u>

SIGNATURE



DATE



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re PATENT APPLICATION of

[illegible]

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Please amend the claims of the above-identified application as follows:

Claim 3, line 1, change “in claim 1 or 2” to -- in claim 1 --.

Claim 4, line 1, change “in claim 1 or 2” to -- in claim 1 --.

Claim 5, line 1, change “in any of claims 1 to 4” to -- in claim 1 --.

Claim 6, line 1, change “in any of claims 1 to 4” to -- in claim 1 --.

Claim 7, line 1, change “in any of claims 1 to 6” to -- in claim 1 --.

Claim 8, line 1, change “in any of claims 1 to 7” to -- in claim 1 --.

Claim 9, line 1, change “in any of claims 1 to 7” to -- in claim 1 --.

Claim 11, line 1, change “in claim 9 or 10” to -- in claim 9 --.

Claim 12, line 1, change "in any of claims 1 to 8" to -- in claim 1 --.

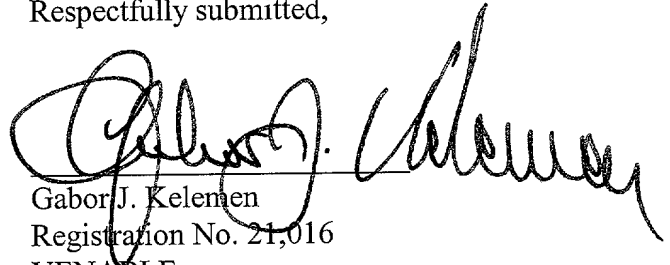
Claim 13, lines 1 & 2, change "in at least one of claims 1 to 12" to -- in claim 1 --.

Claim 15, line 4, change "in any of claims 1 to 12" to -- in claim 1 --.

REMARKS

The claims have been amended to eliminate multiple claim dependency.

Respectfully submitted,



Gabor J. Kelemen

Registration No. 21,016

VENABLE

Suite 1000

1201 New York Avenue, N.W.

Washington, DC 20005-3917

Telephone: (202) 962-4800

Telefax: (202) 962-8300

Correspondence Address:

Venable

P.O. Box 34385

Washington, DC 20043-9998

GJK/rct

#179157

Process for manufacturing an electric conductor with
superconducting cores, and thus manufactured conductor

Technical field

5 The invention relates to a process for
manufacturing an electric conductor with at least two
superconducting cores.

 The cores are frequently also referred to as
filaments. A conductor with several cores or filaments
10 is frequently referred to as a multicore or
multifilament conductor.

Prior art

 WO 96/28 853 A discloses methods for
15 manufacturing electric conductors with several
superconducting cores consisting of ceramic material.
Each core is provided with an inner sheath enclosing it
in cross-section and comprising silver or a silver
alloy, with a casing enclosing the inner sheath and
20 comprising at least one of the metals copper, aluminum,
nickel, iron, magnesium, titanium, zirconium, calcium,
tin, niobium, vanadium, tantalum and hafnium and also
with an outer sheath enclosing the casing and comprising
silver or a silver alloy. A bundle of cores provided
25 with such sheaths and casings is then arranged in a tube
consisting of silver or a silver alloy, lengthened
together with said tube by plastic deformation and
shaped into a tape and subjected to at least one heat
treatment in an oxygen-containing environment. In the
30 latter, a gas exchange, in particular oxygen exchange,
takes place between the cores and the environment. The
ceramic material of the cores is converted into a
superconducting phase, e.g. the phase Bi(2223).
Furthermore, the originally metallic casings should be
35 oxidized in the heat treatment in order electrically to

insulate the cores from one another in the finished conductor.

However, experiments with nickel casings have shown that the casings are damaged during the heat treatment, so that there are in some cases large gaps in the casings. As a result of this, the various cores are electrically insulated from one another only to an insufficient extent. Furthermore, the nickel casings have a disadvantageous effect on the superconducting cores during the heat treatment, in particular their critical temperature or transition temperature being reduced by about 5°C. The damage to the insulating casings and the cores is probably caused by chemical reactions which take place between the materials of the cores and casings with the participation of gas, in particular oxygen, diffusing through the sheaths and casings.

Summary of the invention

It is therefore the object of the invention to provide a process which overcomes disadvantages of the known methods, it being intended in particular to avoid the situation where the casings intended for forming an electrical insulation adversely affects the superconducting properties of the cores and results in only insufficient electrical insulation.

This object is achieved, according to the invention, by a process for manufacturing an electric conductor with at least two elongated, superconducting cores, each of which is enclosed in cross-section by at least one sheath and by a casing, each sheath comprising at least one metallic material and being essentially electrically conducting and the cores, sheaths and casings together being lengthened and together being subjected to at least one heat treatment in an oxygen-

containing environment, characterized in that the casings are formed from a casing material which comprises at least one metal-oxygen compound even before the heat treatment.

5 The invention furthermore relates to an electric conductor with at least two elongated, superconducting cores, which is manufactured by the process.

Advantageous further developments of the subject of the invention are evident from the dependent claims.

10 The cores are preferably formed from a starting core material or core-forming material which comprises a ceramic material and/or is converted into a ceramic material at least by the time of the completion of the conductor, so that the cores of the finished conductor preferably essentially consist of ceramic material.

15 Each core may comprise, for example, oxides of bismuth, strontium, calcium and copper, which, in the finished conductor, consist at least for the most part of a superconducting, textured phase. This can be represented approximately by the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, but may also contain a little lead oxide and/or magnesium oxide and/or titanium oxide and is frequently referred to as Bi(2223) for short. The cores may instead comprise the superconducting phase

20 $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8-x}$, which is denoted by Bi(2212) for short. The cores may furthermore comprise oxides of yttrium or rare earths, barium and copper - for example one of the superconducting phases Y(123) or Y(124) - or oxides of thallium, barium, calcium and copper - or the
25 superconducting phase Tl(1223) or oxides of mercury, barium, calcium and copper.

30 According to the invention, each core is enclosed in cross-section by at least one sheath and by a casing. For example, a sheath arranged between the
35 core and the casing and, for example in addition to this

inner sheath, another outer sheath enclosing the casing or possibly only one sheath enclosing the casing can be provided. Furthermore, for example, a casing directly adjacent to the core and enclosing the latter can be formed for each core, which casing then in turn is enclosed by a sheath.

Each sheath enclosing an individual core and possibly a casing comprises a metallic material and is essentially electrically conducting. Each casing comprises at least one metal oxide and is, at least to a certain extent, electrically insulating or should at least have a substantially greater specific electrical resistance than the sheaths.

The cores serving for the formation of the conductor and provided with sheaths and casings are gathered into a bundle, for example by means of a tube or bundle sheath enclosing them, and, according to the invention, are together lengthened by forming. Forming is preferably effected in a plurality of steps. According to the invention, the cores, sheaths and casings were subjected together - i.e. for example after they were gathered into a bundle by means of a tube or bundle sheath - to at least one heat treatment in an oxygen-containing environment. This or at least one heat treatment serves as reactive annealing in order to form an end core material with the desired, ceramic, superconducting phase from the previously present starting core material or core-forming material by a chemical reaction.

According to the invention, the casings are formed from a casing material which comprises at least one metal-oxygen compound even before the heat treatment. If the cores provided with sheaths and casings and gathered into a bundle are subjected to a plurality of heat treatments, the casing material should

comprise at least one metal-oxygen compound preferably even before the first of these heat treatments and in particular before the or each heat treatment serving for the formation of the superconducting phase - i.e.

- 5 reactive annealing - and namely preferably also before the gathering of the cores into a bundle and before the forming of the cores gathered into a bundle.

Because the casing material comprises at least one metal-oxygen compound even before said heat
10 treatment, it is possible to choose the or each metal-oxygen compound contained in the casing in such a way that it does not react with the core material in the or each heat treatment and that the or each metal-oxygen compound is itself also stable in the or each heat
15 treatment and the casings are also not damaged by the heat treatment(s).

The sheaths and casings should be permeable to oxygen. The sheaths are preferably formed from a sheath material which at least for the most part is metallic
20 and at least for the most part remains metallic and electrically conducting, i.e. is not oxidized, up to the completion of the conductor. The sheath material may, for example, originally consist of pure silver or of silver alloy which, for example, is formed for the most
25 part by weight of silver and additionally contains at least one of the metallic elements, antimony, gold, copper, magnesium, manganese, titanium, aluminum. The proportion of any addition to silver in the sheath material may be, for example, at most equal to or less
30 than 2% by weight in the case of magnesium and/or manganese, at most equal to or less than 0.5% by weight in the case of antimony and at most equal to or less than 10% by weight in the case of gold. While the silver contained in the sheaths and any gold likewise
35 contained therein remains or remain metallic and

electrically conducting during the heat treatment or treatments, any antimony, copper, magnesium, manganese, titanium and/or aluminum contained in the sheaths is oxidized at least to a large extent during the heat treatment or treatments. The sheaths of the finished conductors then consist of a composite having a metallic matrix and oxide islands or oxide particles distributed in said matrix. If each core is enclosed both by an inner and by an outer sheath, the two sheaths may consist of the same or different materials. Furthermore, at least one sheath enclosing an individual core may have two or more layers which consist of different materials.

In an advantageous further development of the process, the or each metal-oxygen compound contained in the casing material consists of a metal oxide or of a compound similar to metal oxide and is binary, ternary, quaternary or quinary. The casing material contains, as the metal-oxygen compound and/or metal oxide, preferably titanate and/or zirconate and/or hafnate and/or magnesium oxide and/or zirconium oxide and/or hafnium oxide and/or bismuth oxide and/or thallium oxide and/or yttrium oxide. The casing material may contain, for example, barium zirconate - BaZrO_3 - and/or barium titanate - BaTiO_3 - and/or the zirconium oxide ZrO_2 . The casing material may furthermore contain, as metal-oxygen compounds or metal oxides, identical or similar ceramic materials, i.e. oxide mixtures, as also used in the formation of superconducting phases - for example phases $\text{Bi}(2212)$, $\text{Bi}(2223)$, $\text{Tl}(1223)$, $\text{Tl}(2223)$, $\text{Y}(123)$, $\text{Y}(124)$. However, the choice and the composition of the casing material must then be tailored to the core material and the operating or use temperature intended for the operation and the use of the conductor in such a way that the critical temperature or transition

temperature of the ceramic material contained in the casing is lower than the critical temperature of the core material and lower than the operating or use temperature of the conductor. If necessary, a small proportion of an additional material which lowers the critical temperature can be added to the ceramic material contained in the casing. The casing material may then also contain, for example, a small proportion of at least one oxide of at least one rare earth and/or of at least one of the elements iron, nickel, cobalt. If such a conductor is then cooled to the intended operating or use temperature, and the cores become superconducting, the casings then remain electrically insulating, as at room temperature.

The casing material or - if, for example, it initially still comprises a liquid and is formed by dispersion - the solid component or phase of the casing material may, for example, originally consist exclusively of at least one metal-oxygen compound.

However, the casing material may originally also comprise, in addition to at least one metal-oxygen compound, a metallic material which preferably contains silver and consists, for example, of pure silver or of a silver alloy. For example, the casing material may contain originally - i.e. before the or each heat treatment - at least one of the metals gold, copper, magnesium, titanium or aluminum, in addition to silver or possibly instead of it. If the casing material provided for the formation of the casings contains silver and/or gold, this is not oxidized during the heat treatment or the heat treatments and is still electrically conducting in the finished conductor. On the other hand, any copper, magnesium, titanium and/or aluminum contained in the casing material is oxidized at least to a large extent during the heat treatment or the

heat treatments in an oxygen-containing environment and then forms oxide islands and/or oxide particles in the casings. The proportion of the metallic material and in particular of the silver and/or gold in the total casing material should be such that the material which is still metallic and electrically conducting in the finished conductor forms no or at least almost no electrically conducting compounds extending from the inner surface of the casing continuously and without interruption to the outer surface thereof. The proportion of any silver and/or gold used for the formation of the casing material and preferably of the total metallic material in the mixture formed from the metallic material and the or each metal oxide is preferably at most 60% by weight, better at most 30% by weight and, for example, about 10% by weight or even less.

The or each metal-oxygen compound contained in the casings is preferably particulate during the formation of the casings, i.e. before the joint forming of the cores provided with sheaths and casings. The particles of the or each particulate metal-oxygen compound of the casing material have particle sizes which are preferably at most 2 μm and, for example, about 0.5 μm or even less.

Any metallic material additionally introduced for the formation of the casings can be mixed with the or each metal-oxygen compound, during the formation of the casing material, in such a way that as homogeneous a mixture as possible forms. The metallic material can, for example, be mixed in the form of particulate metallic material with the or each particulate metal-oxygen compound during the formation of the casing material. The particle sizes of the metallic particles are preferably at most 5 μm and, for example, about 1 μm to 3 μm or even less.

Any silver and/or any metallic materials originally present in the casings and the particles consisting of at least one metal-oxygen compound are possibly separated at least partly from one another during forming and are pressed into various layers. The silver and/or other metallic material is then deposited, for example, on the sheaths present inside and/or outside the casings, so that each casing of the finished conductor then has, for example, a layer consisting predominantly of at least one metal-oxygen compound. The layers formed from the original casings and consisting predominantly of at least one metal-oxygen compound then form the most important part of the casings and hence the actual casings of the finished conductor.

The casings formed at least for the most part or exclusively from at least one metal-oxygen compound are at least to some extent electrically insulating and/or have at least an electrical resistance which, in all directions, is substantially greater than that of an equally thick layer formed from sheath material. The specific electrical resistance of a layer consisting of pure casing material should preferably be at least 10 times, better at least 100 times and, for example, 6000 times greater than that of a layer consisting of pure sheath material. In this context, it should be noted that the core-forming material, the sheath material and the casing material may interpenetrate one another slightly during the forming and during the at least one thermal treatment of the conductor at the originally present boundaries between the cores, sheaths and casings. The electrical resistance of each casing in the direction transverse and approximately at right angles to its longitudinal direction and to the longitudinal direction of the core enclosed by it is

expediently at least 10 times, preferably at least 20 times, even better at least 100 times and, for example, even at least 1000 times greater than the resistance, measured in the same direction, of an equally thick layer coordinated with the relevant core and consisting of sheath material. The electrical resistance between the various cores, measured transverse to the longitudinal direction of the conductor and of the cores, is accordingly, in the case of the conductor according to the invention, expediently at least 10 times, preferably at least 20 times and even better at least 100 times greater than in the case of a conductor not according to the invention, in which the casing is absent and/or has been replaced by a layer of sheath material which has the same shape and the same thickness.

The casings of the finished conductor have a thickness which is preferably at least 0.1 μm , preferably at most 5 μm and, for example, 0.2 μm to 2 μm . It is therefore experimentally difficult directly to measure the electrical resistance and the specific electrical resistance of the casings of a finished conductor. However, it is possible, for example, to pass eddy currents having different frequencies through a conductor and to measure, at various eddy current frequencies, the energy losses caused by eddy currents. The frequency at which the losses are maximum is then a measure of electrical resistance of the sheaths and casings. Comparative measurements of this type between conductors according to the invention and comprising casings and conductors not according to the invention and without casings have shown that the casings result in an increase in the resistance, measured transverse to the cores, in the regions stated in the preceding paragraph.

If each core of the finished conductor is

enclosed by a sheath which is arranged between the core and the casing and is directly adjacent to the core, this sheath bridges, in the longitudinal direction with low longitudinal resistance, any gap in the core enclosed by it.

On the other hand, the various cores of the finished conductor are more or less completely electrically insulated from one another by the casings. A conductor according to the invention can be used, for example, for the formation of a winding of a transformer or of another apparatus. If an eddy current is passed through a conductor according to the invention, no or at most weak current eddies or current loops passing through a plurality of different cores can therefore form. Accordingly, losses of electrical energy due to eddy currents and in particular eddy current coupling losses resulting from the coupling between the various cores can be greatly reduced or even virtually completely avoided.

Brief description of the drawing

The subject of the invention and further advantages thereof are now explained with reference to embodiments shown in the drawing. In the drawing,

Fig. 1 shows a cross-section through an obliquely arranged, cylindrical, rod-like workpiece which serves for forming a core and parts of a conductor which surround said core,

Fig. 2 shows a cross-section through an obliquely arranged workpiece having a hexagonal cross-section and formed by forming the workpiece shown in Fig. 1,

Fig. 3 shows a cross-section of a starting conductor comprising workpieces formed according to Fig. 2,

Fig. 4 shows a schematic end view of a part of the

conductor having 19 cores and formed by forming the starting conductor shown in Fig. 3,

Fig. 5 shows a photographed cross-section through a partly formed conductor having 30 cores,

5 Fig. 6 shows a photographed cross-sectional region of the conductor shown in Fig. 5, after the forming and after the complete thermal treatment,

Fig. 7 shows a schematic end view of a part of a conductor which was formed from workpieces without an
10 outer sheath,

Fig. 8 shows a view, analogous to Fig. 2, of a workpiece in which the casing is directly adjacent to the core, and

Fig. 9 shows a simplified end view of a conductor
15 having cores which have differently oriented broad sides.

Description of the preferred embodiments

For the manufacture of a conductor, for example
20 a ribbon-like one, having a plurality of superconducting cores, for example containing the phase Bi(2223), oxides and carbonates of the metals bismuth, lead, strontium, calcium and copper are provided as starting materials. For example, the following oxides and carbonates may be
25 used: Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO . However, it should be noted that other oxides and carbonates or precursor substances thereof may also be used.

The oxides and carbonates are processed by precipitation and/or milling to give a fine-particled
30 powder and are mixed with one another to give a powder mixture which serves as particulate core-forming material. The ratios of the various oxides and carbonates are established on mixing so that the core-forming material contains the metal atoms, for example,
35 in the composition $\text{Bi}_{1.72}$, $\text{Pb}_{0.34}$, $\text{Sr}_{1.83}$, $\text{Ca}_{1.97}$, $\text{Cu}_{3.13}$.

The particulate, originally electrically nonconducting starting core material or core-forming material is calcined at least once and, for example, several times for several hours at a temperature of about 800°C in an air-containing environment. During the calcination, some of the particulate mixture may be converted into the crystalline phase Bi(2212) by a reaction. The calcined core-forming material is milled.

A rod-like workpiece 1 shown in Fig. 2 is then produced for each conductor core to be formed. This has an inner starting sheath 4 formed from a hollow cylindrical tube. Said sheath encloses, in cross-section, a starting core 3 consisting of particulate starting core material or core-forming material. The interior of the inner starting sheath 5 is closed at both ends so that the particulate core-forming material does not fall out and can absorb neither water nor carbon dioxide from the surrounding air. The inner starting sheath 5 is enclosed in cross-section by a casing 5. The casing 5 is enclosed in cross-section in turn by an outer starting sheath 6.

The starting sheaths 4 and 6 consist, for example, of pure silver or one of the other materials which are stated in the introduction and can be used for forming sheaths. In the production of the workpieces 1, for example, an inner starting sheath 4 and an outer starting sheath 6 are first formed for each workpiece. These starting sheaths are cut, for example, from commercially available, longer tubes.

For the formation of the casings 5, for example, pure particulate barium zirconate (BaZrO_3) and pure, particulate silver are prepared or acquired. Particulate barium zirconate is then mixed with particulate silver so that as homogeneous a mixture as possible forms, which contains, for example, about 10%

by weight of silver. This mixture is also mixed, for example, with a liquid which, for example, consists at least to a large extent or completely of alcohol or another organic solvent and/or dispersant. The liquid-
5 solid mixture or suspension formed is then applied to the outer surface of the inner starting sheath 4, for example with the aid of a brush or by spraying on, so that the casing material forms a coating adhering to the inner starting sheath 4. The inner starting sheath 4
10 coated with a starting casing 5 and the outer starting sheath 6 are then inserted one into the other. The liquid solvent and/or dispersant which serves for forming the casings then evaporates and/or vaporizes again so that only the solid casing material is left.

15 That component or phase of the casing material serving for forming the casings which is formed from solid particles, and the casing material remaining after the solvent and/or dispersant has escaped, may consist exclusively of BaZrO_3 or another casing material stated
20 in the introduction, instead of consisting of a BaZrO_3 -silver mixture.

There are also other possibilities for introducing the casing material between the inner and outer sheaths. For example, the sheaths 4 and 6 having
25 no casing material can be inserted one into the other and, at the same time and/or afterward, dry, pulverulent casing material can be introduced between the two sheaths.

Before or after the starting sheaths 4 and 6
30 have been inserted one into the other, particulate, calcined and milled core-forming material is filled into the interior enclosed by the inner starting sheath 4 and the starting core 3 is thus formed. The inner cavity of the inner starting sheath 4 is then closed at both ends.

35 Each inner starting sheath 4 has, for example,

an external diameter of 5 mm to 10 mm. The internal diameter of each inner starting sheath and the diameter of the starting core 3, which is identical to this internal diameter, is, for example, 50% to 80% of the external diameter of the inner starting sheath 4. The radially measured thickness of the casing 5 is substantially smaller than the correspondingly measured thickness of the inner starting sheath 4.

Each elongated, cylindrical workpiece 1 is formed, for example, by drawing and/or pressing to give the workpiece which is shown in Fig. 2, has the shape of a regular hexagon in cross-section and is likewise denoted by 1. This forming is preferably carried out by cold-forming, i.e. at normal room temperature. The workpiece 1 becomes longer and thinner during this forming and is then rod-like and or wire-like.

Furthermore, a starting bundle sheath 8 shown in Fig. 3 is produced, for example cut from a longer tube. The sheath 8 consists, for example, of pure silver or another sheath-forming material stated in the introduction. The starting bundle sheath 8 is, for example, a hollow cylinder.

Workpieces 1 having a hexagonal cross-section are inserted into the starting bundle sheath 8 so that they form a workpiece bundle 11 held together by said sheath. The workpieces rest with pairs of their surfaces against one another and together form a "close packing" which fills the interior of the starting bundle sheath 8 as substantially as possible. the starting bundle sheath 8 may contain, for example, 9 or 19 or 37 or an even larger number, permitting "close packing", of workpieces 1. The dimensions of the workpieces 1 and of the starting bundle sheath 8 are, for example, tailored to one another so that the "close packed" workpiece bundle fits into the sheath 8 in such a way that some

workpieces distributed around the axis of the bundle 11 and forming apices of a regular envelope polygon surrounding said bundle rest tightly or with at most little play against the cylindrical inner surface of the starting bundle sheath 8. The workpiece bundle 11, together with the starting bundle sheath 8, then form a starting conductor denoted by 21. The diameter or - more precisely - external diameter of the starting conductor is preferably at least 20 mm and, for example, 40 mm to 120 mm.

The starting conductor 21 and the cores 3, sheaths 4, 6 and casings 5 present therein are now formed, i.e. lengthened, in a plurality of steps. The cross-sectional area of the conductor is gradually reduced, and the interior spaces which are shown in Fig. 3 and are present in the starting bundle sheath 8 and empty, i.e. contain only air, disappear.

The starting conductor 21 having a cylindrical outer surface is first formed, for example, by extrusion and/or hammering and/or drawing to give an intermediate conductor which is wire-like, i.e. still approximately or exactly circular in cross-section. This intermediate conductor is possibly rotated about its longitudinal axis so that the conductor parts originally formed by the workpieces 1, and the cores of said conductor parts, are twisted. The intermediate conductor having straight, parallel or twisted cores is now rolled in a plurality of rolling operations and is formed into an elongated, ribbon-like conductor. The forming of the starting conductor 1, first effected by extrusion, is then carried out, for example, by hot forming, the temperature during the hot forming being substantially less than 800°C. The remaining forming steps can then be carried out, for example, by cold forming, i.e. at normal room temperature. However, the conductor may be

formed, at least during the final rolling operation or during the final rolling operations or even during all rolling operations, by hot forming at a temperature of, for example, 500°C to 800°C.

5 The metallic sheaths 4, 6, 8 are ductile and are plastically deformed during forming of the conductor. The core material consists, at least originally, of individual particles which, during the forming of the conductor, are both pushed against one another and
10 individually more or less plastically deformed, restructured and textured. Any metallic material contained in the casings 5 is plastically deformed during the forming of the conductor. Those particles of the casings 5 which consist of a metal-oxygen compound,
15 for example of barium zirconate, are in particular pushed against one another and possibly also individually plastically deformed during the forming of the conductor. Otherwise, the particles present in the cores and/or those present in the casings are possibly
20 bonded to one another more or less firmly, for example sintered together to a certain extent, by the pressure and/or the heat during the forming and the subsequent heat treatments described in more detail.

 Between successive forming steps and/or after
25 the end of the forming, the conductor is subjected to at least one heat treatment - i.e. reactive annealing - in an oxygen-containing environment. Reactive annealing is carried out in particular between the penultimate and the final rolling operation. Preferably, however, at
30 least one heat treatment each takes place before the penultimate rolling operation and after the final rolling operation. In the or each reactive annealing, the conductor is heated to a temperature of at least 790°C, preferably at least 800°C and, for example, 820°C
35 to 830°C or up to 840°C. During the reactive annealing

or the reactive annealings, the conductor is annealed, for example, for at least 100 hours in a gas mixture containing, for example, 0.1% by volume to 20% by volume of oxygen or possibly in air.

5 During these heat treatments, the material of the cores of the conductor is converted in a manner known per se, at least to a major extent and virtually completely, into the phase Bi(2223). The heat treatments are also accompanied by a gas exchange, in
10 particular an oxygen exchange, in which the cores release and/or absorb gas, in particular oxygen, through the sheaths consisting at least partly of silver and through the casings.

 The starting core 3, the starting sheaths 4, 6
15 and the starting casing 5 of the originally cylindrical workpieces 1 are lengthened, for example at least 10 times, during the forming of said workpieces into hexagonal workpieces and during the subsequent forming of the starting conductor 21. The cross-sectional areas
20 of the workpieces 1 are reduced by a factor which is approximately equal to the square of the lengthening factor.

 The finished, elongated conductor produced by the process described and shown in Fig. 4 is denoted by
25 21, similarly to the starting conductor shown in Fig. 3. Furthermore, the cores, inner sheaths, casings, outer sheaths and the bundle sheath of the finished conductor in Fig. 4 are also denoted by the same numbers as the corresponding starting parts in Fig. 3.

30 The finished conductor 21 shown in Fig. 4 is ribbon-like and approximately rectangular in cross-section and has two broader, essentially flat and parallel surfaces 21a facing away from one another and two narrower, possibly likewise at least partly flat
35 and/or at least partly convex surfaces 21b facing away

from one another. Those cores 3 of the finished conductor which were formed from the starting cores 3 are superconducting at sufficiently low temperatures. Each core 3 of the finished conductor is enclosed in cross-section by an electrically conducting sheath 4. Each sheath 4 of the finished conductor is surrounded in cross-section by an electrically insulating, oxygen-permeable casing 5 consisting, for at least the most part, of barium zirconate. In the various forming steps, the outer sheaths 6 and the bundle sheath 8 were at least substantially connected to one another in such a way that they are virtually cohesive in the finished conductor and form an electrically conducting matrix denoted by 29 in Fig. 4. The contours of the outer sheaths 6 are therefore indicated only by dash-dot lines in Fig. 4. In Fig. 4, the cores 3 are drawn schematically as rectangles whose broader sides are parallel to the broader surfaces 21a of the ribbon-like conductor 21. However, it should be noted that the cores 3, in an end view and in cross-section, actually have shapes which are more irregular and differ from rectangles. The same applies to the sheaths 4 and 6 and the casings 5.

The width, i.e. the larger cross-sectional dimension of the finished conductor 21 measured parallel to the flat sections of the broader surfaces 21a, is preferably at least 1 mm, and, for example, 2 mm to 10 mm. The thickness of the conductor 21, measured at right angles to the width, is preferably at most 30% and, for example, about 5% to 20% of the width, for example 0.1 mm to 0.5 mm.

The widths, i.e. the larger cross-sectional dimensions of the cores 3 measured parallel to the broader surfaces 21a of the finished conductor 21, are, for example, about 30 μm to 150 μm . The thicknesses,

i.e. the smaller cross-sectional dimensions of the cores measured at right angles to the surfaces 21, are, for example, in the range from 5 μm to 20 μm . The inner sheaths 24 have, for example, thicknesses of a few micrometers. The thicknesses of the insulating casings are, for example, in the range from 0.1 or 0.2 μm to 2 μm or possibly to 5 μm .

The conductor 21 photographed in various phases of the process in Figures 5 and 6 was manufactured by a process similar to that described with reference to Figures 1 to 4, but is formed from 30 workpieces corresponding to the workpieces 1 and accordingly contains 30 cores 3. Fig. 5 shows the state of the partly, but not yet completely, formed conductor after some rolling operations, before the reactive annealing or the reactive annealings. Fig. 6 shows a section of the finished conductor 21, which after the complete forming and after the or each reactive annealing of the conductor. The inner sheaths and the casings are denoted by 4 and 5, respectively, in Figures 5 and 6, as in Figures 1 to 4. In the case of the conductor 21 shown in Figures 5 and 6, the original outer sheaths 6 and the original bundle sheath 8 together once again form a more or less cohesive matrix 29.

Investigations have shown that the casings 5 of the finished conductor which are formed from barium zirconate and silver or exclusively from barium zirconate or at least essentially from magnesium oxide (MgO) - in contrast to the casings which are disclosed in WO 96/28 853 A, consist originally of nickel and then oxidized - have no unfavorable effects at all on the superconducting properties of the cores during the heat treatments and the remaining process of manufacture. It was found in particular that the transition temperature or critical temperature of the cores is not lowered by

the casings according to the invention in comparison with the conductors without such casings. Similarly, microscopic investigations of sections through conductors according to the invention have shown that

5 the casings 5 enclose the internal sheaths 4 and hence also the cores 3 in cross-section over the entire length of the conductor, at least almost without gaps and completely.

The elongated, ribbon-like conductor shown in

10 Fig. 7 has a plurality of cores 33 which are superconducting when the conductor is used. Each core 33 is enclosed in cross-section by an electrically conducting sheath 34 which in turn in cross-section is surrounded by an electrically insulating casing 35. The

15 conductor 31 furthermore has a bundle sheath 38 which encloses the bundle of the cores 33 and the sheaths 34 coordinated with them, as well as casings. The conductor 31 has no outer sheaths corresponding to the outer sheaths 6 of the conductor 21, so that, in the

20 conductor 31, casings 35 coordinated with different cores 33 abut one another.

The workpiece 41 shown in Fig. 8 was formed in the same way as the workpiece 1 shown in Fig. 2, so that it is hexagonal in cross-section. The workpiece 41 has

25 a core 43, a casing 45 enclosing said core and directly adjacent to said core, and a sheath 46 enclosing said casing, but no sheath corresponding to the inner sheath 4 of the workpieces 1. It is possible to produce a plurality of workpieces 41 and to form a conductor

30 therefrom analogously to the formation from workpieces 1.

The conductor 51 shown in Fig. 9 is in an intermediate phase of the manufacturing process and has a plurality of workpieces 61 which are rectangular in

35 cross-section and are shown only in simplified form.

Each of said workpieces 61 has, as in the case of a workpiece 1, for example, a core, an inner sheath, a casing enclosing the core and the inner sheath, and an outer sheath, but may also have a structure analogous to that of the workpieces serving for the formation of the conductor 31 or analogous to that of the workpiece 41. The conductor 51 furthermore has a bundle sheath 68 whose outer surfaces form the outer surfaces of the entire conductor 51. The workpieces 61 are divided into a middle group and two lateral groups arranged on sides of said middle group which face away from one another. Each lateral group contains half as many workpieces as the middle group. The broad sides of the workpieces of the middle group are parallel to the broad sides or broader outer surfaces of the entire conductor. The broad sides of the workpieces of the two lateral groups are parallel to the narrow sides or narrower outer surfaces of the entire conductor. A finished conductor can be formed from the conductor 51 shown in an intermediate state in Fig. 9, by forming and at least one heat treatment. Said finished conductor then contains a middle group of cores and two lateral groups of cores whose broad sides are generally approximately parallel or approximately at right angles to the broader outer surfaces of the conductor.

The conductors and the process for their manufacture can also be modified in other ways. For example, in the forming of a starting conductor to give a finished conductor, the rolling can be replaced by drawing so that the finished conductor is roundish and is, for example, approximately or exactly circular in cross-section or, for example, approximately forms a regular hexagon.

Reference is once again made to WO 96/28 853 A which was cited above and whose content is hereby

incorporated in the present Patent Application, provided that there are no contradictions.

PATENT CLAIMS

1. A process for manufacturing an electric conductor (21, 31, 51) with at least two elongated, superconducting cores (3, 33, 43), each of which is enclosed in cross-section by at least one sheath (4, 6, 34, 46) and by a casing (5, 35, 45), each sheath (4, 6, 34, 46) comprising at least one metallic material and being essentially electrically conducting, and the cores (3, 33, 43), sheaths (4, 6, 34, 46) and casings (5, 35, 45) together being lengthened by forming and together being subjected to at least one heat treatment in an oxygen-containing environment, characterized in that the casings (5, 35, 45) are formed from a casing material which already comprises at least one metal-oxygen compound before the heat treatment.

2. The process as claimed in claim 1, characterized in that the casing material used for the formation of the casings (5, 35, 45) contains, as the metal-oxygen compound, a metal oxide and/or titanate and/or zirconate and/or hafniate.

3. The process as claimed in claim 1 or 2, characterized in that the casing material used for the formation of the casings (5, 35, 45) contains, as the metal-oxygen compound, magnesium oxide and/or zirconium oxide and/or hafnium oxide and/or bismuth oxide and/or thallium oxide and/or yttrium oxide.

4. The process as claimed in claim 1 or 2, characterized in that the casing material used for the formation of the casings (5, 34, 45) contains, as the metal-oxygen compound, barium zirconate (BaZrO_3) and/or barium titanate (BaTiO_3) and/or the zirconium oxide (ZrO_2).

5. The process as claimed in any of claims 1 to 4, characterized in that a sheath (4, 34) directly adjacent to the core (3, 33, 43) and enclosing said core and the casing (5, 35) enclosing said sheath are formed for each core (3, 33, 43).

6. The process as claimed in any of claims 1 to 4, characterized in that a casing (45) directly adjacent to the core (43) and enclosing said core and a sheath (46) enclosing said casing are formed for each core (43).

7. The process as claimed in any of claims 1 to 6, characterized in that the or each metal-oxygen compound contained in the casing material is particulate during the formation of the casings (5, 35, 45), the or each particulate metal-oxygen compound preferably being formed in the form of solid particles which preferably have a particle size of at most 2 μm before the beginning of the forming of the conductor (21, 31, 51).

8. The process as claimed in any of claims 1 to 7, characterized in that the casing material used for the formation of the casing (5, 35, 45) has a solid phase or is completely solid, and that the solid phase or the solid casing material consists exclusively of at least one metal-oxygen compound.

9. The process as claimed in any of claims 1 to 7, characterized in that the or each metal-oxygen compound is mixed with particulate, metallic material during the formation of the casing material.

10. The process as claimed in claim 9, characterized in that the metallic material serving for the formation of the casing material comprises silver and, for

example, consists of pure silver and/or of a silver alloy.

11. The process as claimed in claim 9 or 10, characterized in that the proportion of silver in the mixture consisting of at least one metal-oxygen compound and metallic material and/or in the casings (5, 35) of the finished conductor is at most 60% by weight, preferably at most 30% by weight and, for example, about or at most 10% by weight.

12. The process as claimed in any of claims 1 to 8, characterized in that each core (3, 33) comprises ceramic material, at least in the finished conductor.

13. The process as claimed in at least one of claims 1 to 12, characterized in that the sheaths (4, 6, 34, 46) are formed from a sheath material which consists at least partly of silver.

14. The process as claimed in claim 13, characterized in that the sheaths (4, 6, 34, 46) are formed from a sheath material which for the most part by weight consists of silver and also contains at least one of the elements antimony, gold, copper, magnesium, manganese, titanium, aluminum.

15. An electric conductor with at least two elongated, superconducting cores (3, 33), characterized in that said conductor is manufactured by the process as claimed in any of claims 1 to 12.

ABSTRACT

For manufacturing the electric conductor (21), workpieces are formed, each of which has a core (3) which is enclosed in cross-section by at least one electrically conducting sheath (4, 6) and a casing (5) which consists at least partly of at least one metal-oxygen compound, for example barium zirconate (BaZrO_3). The workpieces are gathered into a bundle, lengthened together by plastic deformation and subjected to at least one heat treatment in an oxygen-containing environment. During the heat treatment or the heat treatments, the material forming the cores (3) is converted into a superconducting phase without the superconducting properties of the cores (3) being adversely affected by the casing material. The casings (5) are electrically insulating or have at least a substantially higher specific electrical resistance than the sheaths (4) and, during the use of the conductor (21), counteract the formation of eddy current coupling losses.

(Fig. 4)

Fig. 1

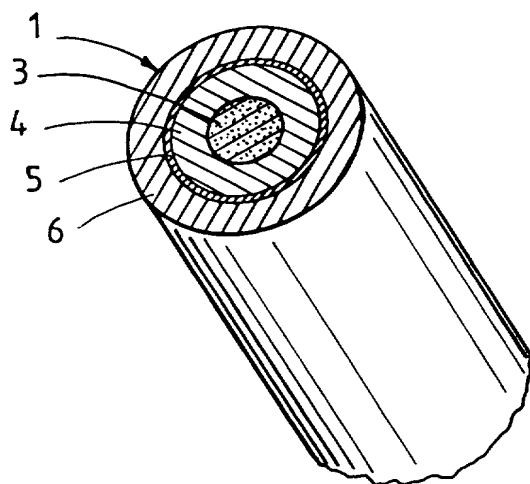


Fig. 2

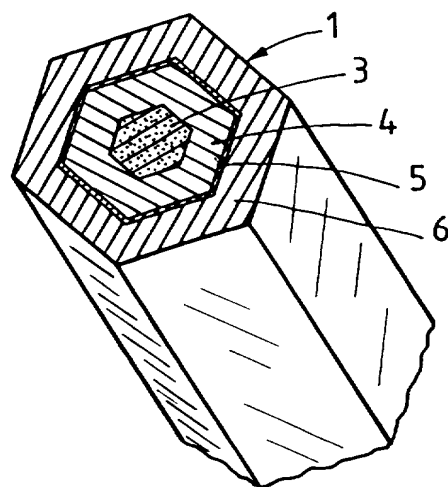


Fig. 3

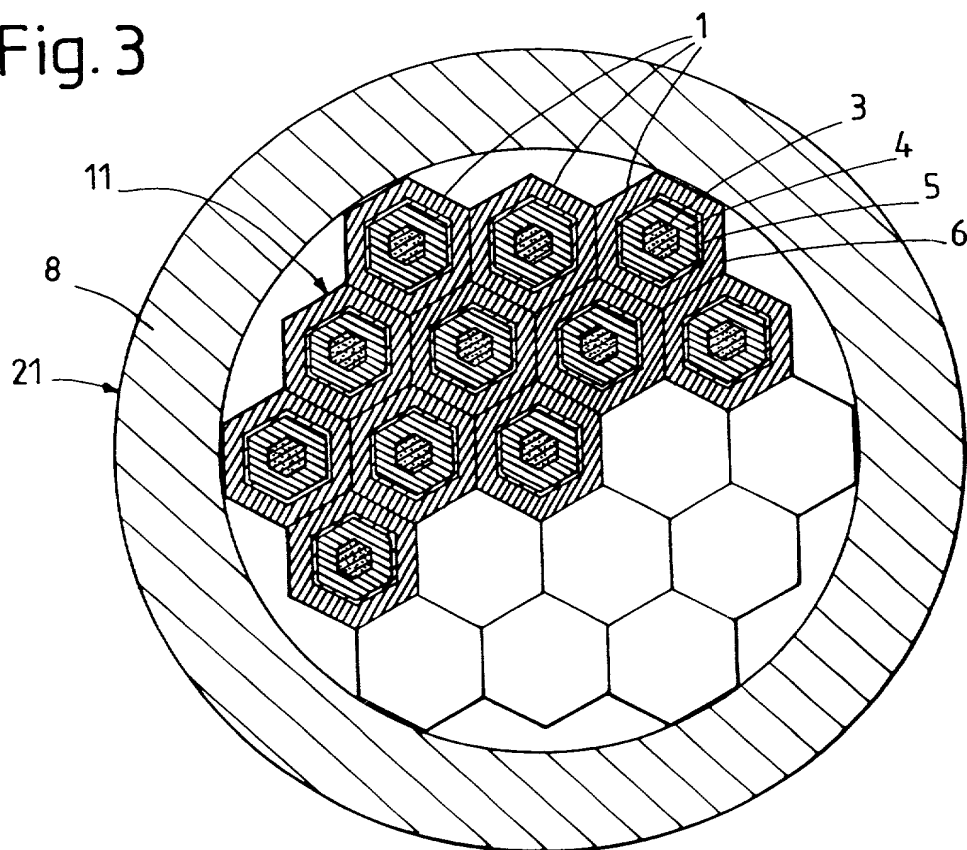


Fig. 4

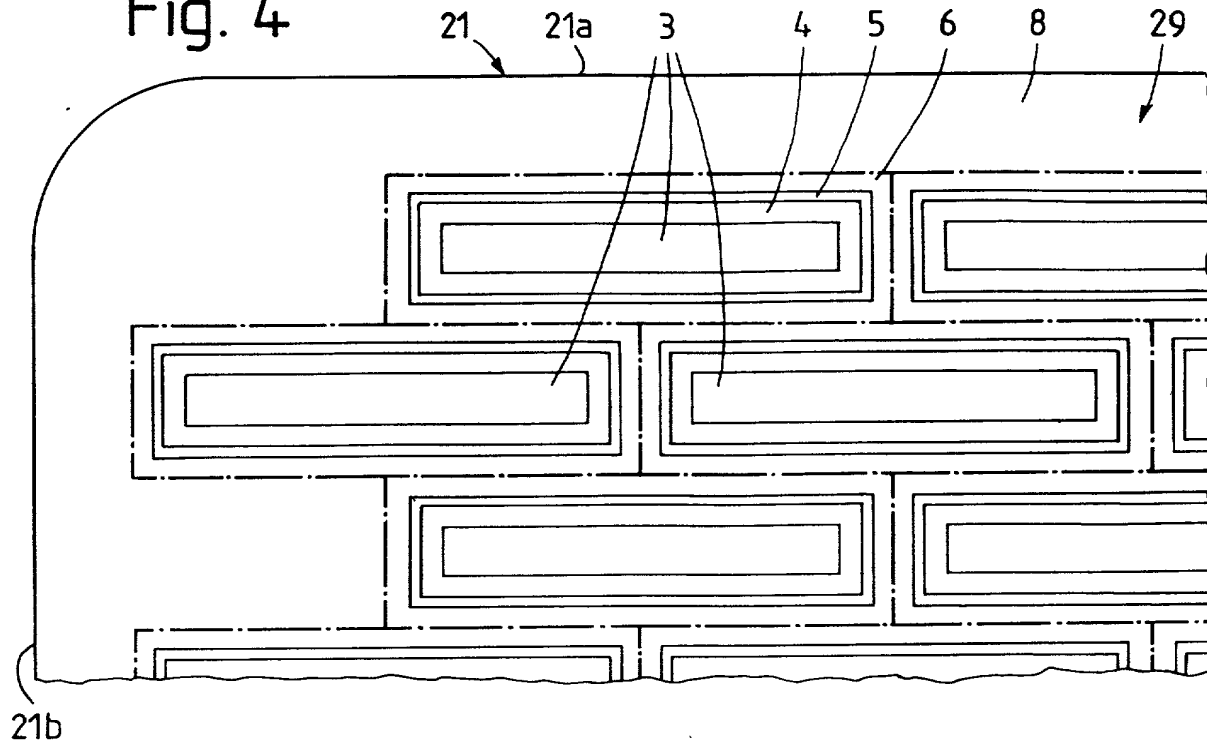


Fig. 7

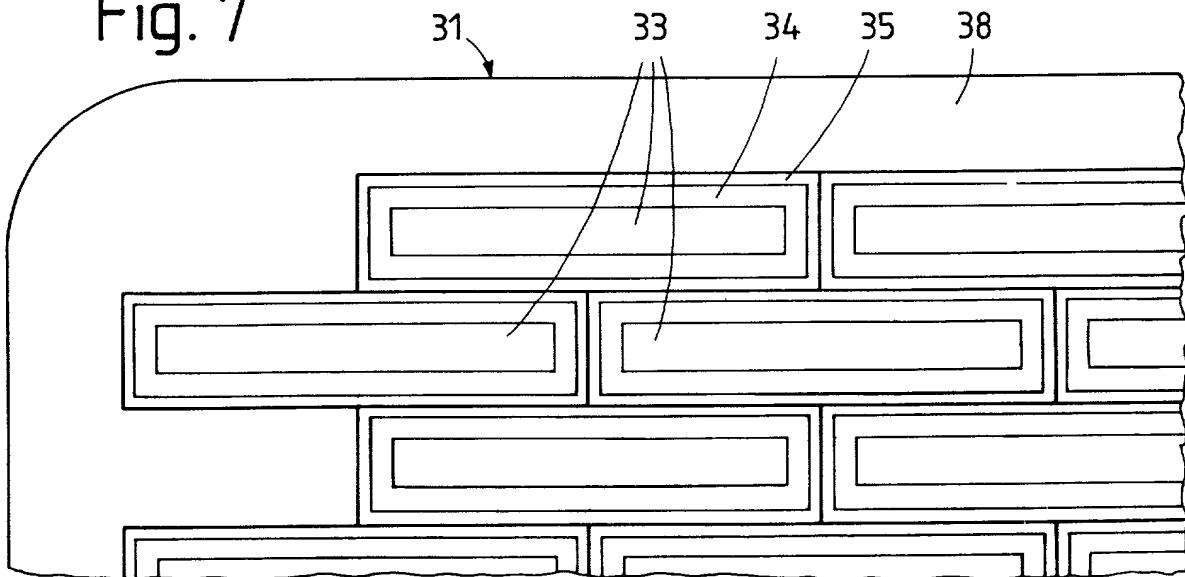


Fig. 8

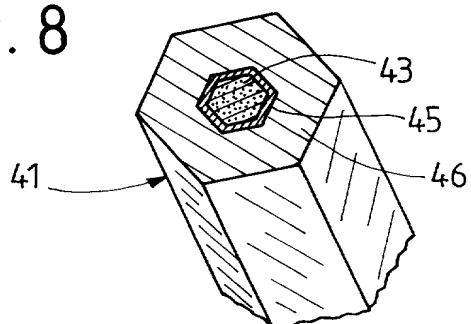


Fig. 9

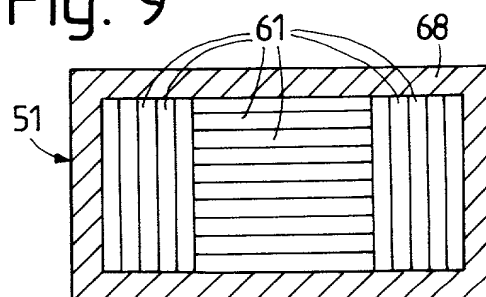


Fig. 5

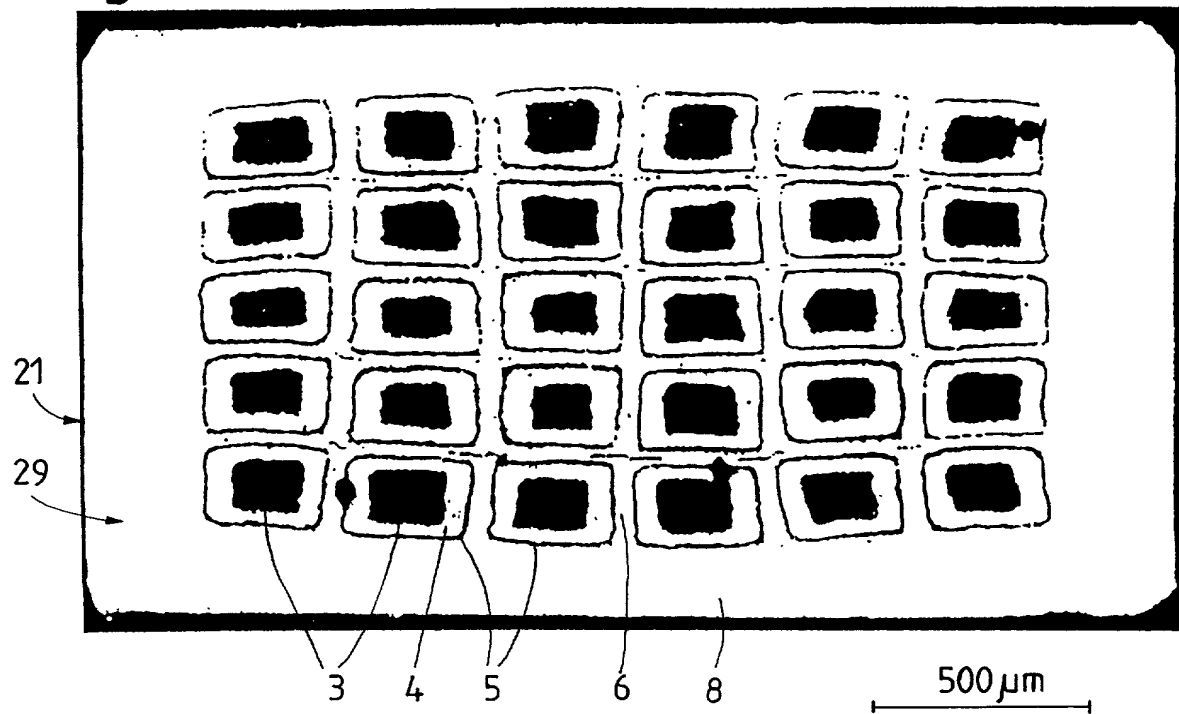
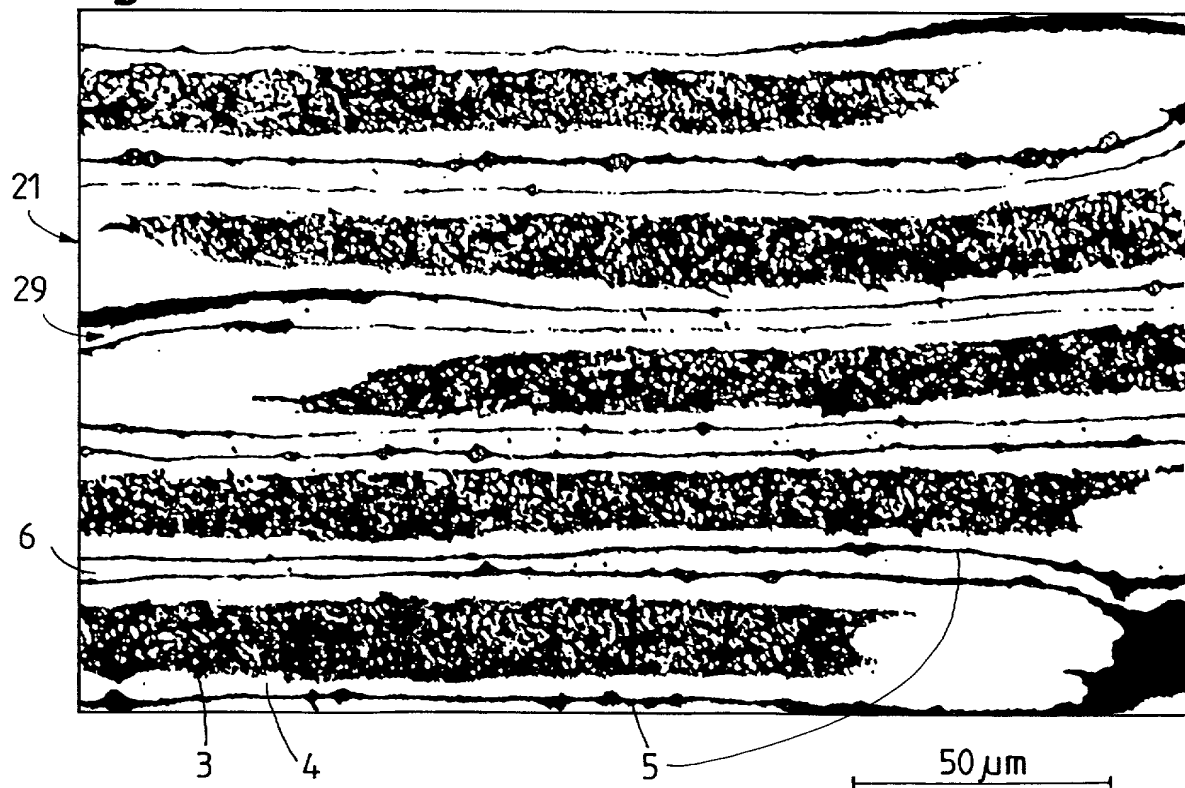


Fig. 6



DECLARATION FOR UNITED STATES PATENT APPLICATION,
POWER OF ATTORNEY, DESIGNATION OF CORRESPONDENCE ADDRESS

Attorney Docket
31506-149973

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and that I believe I am an original, joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled PROCESS FOR MANUFACTURING AN ELECTRIC CONDUCTOR WITH SUPERCONDUCTING CORES, AND THUS MANUFACTURED CONDUCTOR, the specification of which was filed under the Patent Cooperation Treaty on December 19, 1997, Serial No. PCT/CH97/00475, the United States of America being designated.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent, utility model, design or inventor's certificate listed below and have also identified below any foreign application(s) for patent, utility model, design or inventor's certificate having a filing date before that of the application(s) on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
Number	Country	Date Filed	Yes	No
3141/96	Switzerland	December 20, 1996	X	

9 I hereby appoint the following attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: George H. Spencer (Reg. No. 18,038), Norman N. Kunitz (Reg. No. 20,586), Robert J. Frank (Reg. No. 19,112), Gabor J. Kelemen (Reg. No. 21,016), Robert Kinberg (Reg. No. 26,924), John W. Schneller (Reg. No. 26,031), Ashley J. Wells (Reg. No. 29,847), Allen Wood (Reg. No. 28,134), James R. Burdett (Reg. No. 31,594) Suite 1000, 1201 New York Avenue, N.W., Washington, D.C. 20005-3917, Telephone: (202) 962-4800, Telefax: (202) 962-8300.

Address all correspondence to VENABLE, P.O. Box 34385, Washington, D.C. 20043-9998.

The undersigned hereby authorizes the U.S. attorneys named herein to accept and follow instructions from the undersigned's assignee, if any, and/or, if the undersigned is not a resident of the United States, the undersigned's domestic attorney, patent attorney or patent agent, as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and the undersigned. In the event of a change in the person(s) from whom instructions may be taken, the U.S. attorneys named herein will be so notified by the undersigned.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signature: René L.J. Flükiger Date: Geneva, 24.11.99
First Joint Inventor: Prof. René L.J. Flükiger
Citizenship: Switzerland
Residence and Post Office Address: 42, chemin de la Plamatte,
1228 Plan-Les-Quates
Switzerland CHX

VENABLE
Washington, D.C.

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DECLARATION FOR UNITED STATES PATENT APPLICATION,
POWER OF ATTORNEY, DESIGNATION OF CORRESPONDENCE ADDRESS

Attorney Docket
31506-149973

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2nd $\frac{9}{10} - \frac{1}{2}$
Signature: _____ Date: Wrexham, 06/12/99
Second Joint Inventor: Dr. Ybing (also known as Yibing) Huang
Citizenship: China
Residence and Post Office Address: 22 The Triangle
Wrexham LL13 9NJ GBX
Great Britain

Signature: [Signature] Date: Genova, 1.12.1999
Third Joint Inventor: Dr. Giovanni Grasso
Citizenship: Italy
Residence and Post Office Address: Via Barrili 2A/7A
IT-16143 Genova
Italy

#153376